

# Critical temperature and upper critical field of $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$ ( $x=0.0, 0.1, 0.2$ ) superconductors

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## Abstract

We studied the effects of substitution of Pd by Cu on the upper critical field of the noncentrosymmetric superconductor  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$ , with  $x=0.0, 0.1$  and  $0.2$ . The upper critical field as a function of temperature was determined by resistance measurements at different magnetic fields. We found that the superconducting transition temperature decreases as the Cu content increases. Moreover, the temperature dependence of the upper critical field is linear in the range of the temperature studied and, at low temperature, is enhanced compared with the prediction of the Werthamer-Helfand-Hohenberg theory. This indicates that the breaking of Cooper pairs by spin orbit scattering and Pauli paramagnetism is negligible, and that the upper critical field enhancement is mainly because the electron-phonon coupling and disorder.

**Keywords:** A. Noncentrosymmetric superconductor, C.  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$ , D. Upper critical field

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## 1. Introduction

Noncentrosymmetric superconductors present a nonstandard superconducting behavior. The absence of inversion symmetry produces an antisymmetric spin-orbit coupling (ASOC) that modify the electronic behavior, and Cooper pairs tend to pair in a mixture of spin-singlet and spin-triplet symmetry depending of the ASOC intensity, producing nodes or lines of nodes in the energy gap function [1–4].

The noncentrosymmetric superconductor  $\text{Li}_2\text{Pd}_3\text{B}$  is considered a conventional superconductor without strong electronic correlations [2, 3, 5], with transition temperature about  $T_C \sim 7\text{--}8\text{ K}$ . The substitution of Pd with Pt induces important changes, for example, the  $T_C$  value decreases to  $2.2\text{ K}$  and the system displays a mixture of spin-singlet and spin-triplet pairing; thus the superconducting energy gap function has lines of nodes [4, 6, 7].

Substitution of elements in  $\text{Li}_2\text{Pd}_3\text{B}$  modifies its electronic characteristics, particularly the substitution of Pd renders modifications of the electronic density of states (DOS) and in consequence the superconducting properties, because the Pd  $4d$  electrons are considered responsible of superconductivity [5, 8, 9]. Partial substitution of Pd with Ni, produces a decrement of  $T_C$  and upper critical field at  $T = 0\text{ K}$  ( $H_{C2}(0)$ ) as the Ni content increases [5, 8, 10]. Substitution with a nonmagnetic element, as Al in the B sites, causes a decrement of  $T_C$  but  $H_{C2}(0)$  becomes increased by a factor of  $1.5$  [11]. It is noteworthy that in both substitutions  $H_{C2}(T)$  shows a linear behavior in the temperature and in the impurity range studied. The linear behavior of  $H_{C2}(T)$  has been observed in two band superconductors [12–14] and in isotropic gaped superconductors [15].

The Werthamer-Helfand-Hohenberg (WHH) theory [16, 17] provides a way to study the effects of the spin paramagnetism and the spin-orbit scattering on the upper critical field behavior of superconducting materials. This theory takes into account the Cooper pair breaking with the Pauli paramagnetism and the spin-orbit scattering. The presence of these processes produce a decrement of  $H_{C2}(T)$  at low temperatures, as compared with the upper critical field when they are not present, and it is linear near  $T_C$ .

Until now, a study of the effect of substitution of Pd with Cu, a nonmagnetic element, has not be reported yet. In this paper we report the effects of partial substitution of Pd with Cu on the critical temperature and on the temperature

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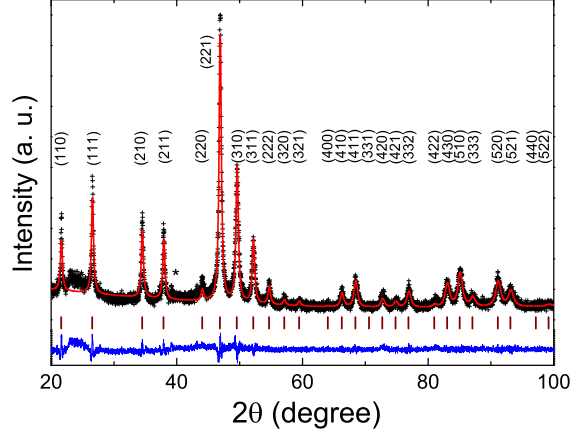


Figure 1: (Color online) X-ray patterns of  $\text{Li}_2\text{Pd}_{3-x}\text{B}$  and Rietveld refinement (continuous line). Vertical lines are the reflections, reflection at  $39.3^\circ$  corresponds to a tiny amount of  $\text{Pd}_2\text{B}_5$  impurity. The line at the bottom is the difference between experimental and refined pattern.

dependance of the upper critical magnetic field of  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  with  $x=0.0, 0.1$  and  $0.2$ . The results show that  $T_C$  decreases with the Cu increment faster than when Pd is substituted with a magnetic element. Forward,  $H_{C2}(T)$  shows a linear behavior and enhances at low temperatures deviating from the WHH theory. This behavior indicates that the spin-orbit scattering and the Pauli paramagnetism take a minor role in the Cooper pairs breaking.

## 2. Experimental details

Polycrystalline samples of  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  with  $x=0.0, 0.1$  and  $0.2$ , were synthesized by arc-melting using Li (99+%), Pd (99.95%), Cu (99.99%) and B (99.99%) powders as precursors. The synthesis was performed in argon atmosphere, following the two-step process as reported by Togano et al. [18] and adding 20% Li excess to compensate losses. The obtained ingots were processed several times in order to get homogeneous samples. Sample structure was determined by X-Ray diffraction, X-ray patterns of the powdered samples were acquired at room temperature using a Siemens D-5000 diffractometer with  $\text{Co-K}_\alpha$  radiation ( $\lambda = 1.79026 \text{ \AA}$ ) and Fe filter. Patterns were obtained in steps of  $0.015^\circ$  at 8 s in the  $2\theta$  range of  $20^\circ$  to  $100^\circ$ . Rietveld analysis of diffraction patterns was performed with the MAUD program [19].

Electrical resistance versus temperature ( $R(T)$ ) and magnetic field was measured using the four-probe technique in a Physical Properties Measurement System (Quantum Design).  $R(T)$  measurements, without applied magnetic field, were measured from room temperature to 2 K. The magnetoresistance measurements were performed between 2 K and 10 K with applied magnetic field between 0 and 40 kOe.

## 3. Results and discussion

As mentioned, the  $\text{Li}_2\text{Pd}_3\text{Cu}_x\text{B}$  samples were analyzed by X-ray powder and diffraction patterns fitted by Rietveld method, Fig. 1 shows the refined pattern of  $\text{Li}_2\text{Pd}_{3-x}\text{B}$  sample. Vertical lines, at the bottom of the panel, are the reported reflections (ICSD 84931), where the Miller indexes of each plane are indicated. Tiny amount of impurities of  $\text{Pd}_2\text{B}_5$  was identified in the sample, it is indicated with \*. The difference between the experimental pattern and the refined pattern is show at the bottom of the figure. Refinements were performed using the space group  $P4_332$  as used in previous reports [8, 20, 21]. Lattice parameters of the cubic structure obtained from the Rietveld analysis are:  $6.7427(2) \text{ \AA}$ ,  $6.7363(2) \text{ \AA}$  and  $6.7401(2) \text{ \AA}$  for  $x=0, 0.1$  and  $0.2$ , respectively. The value obtained for the sample without Cu is in agreement to reported values [8, 18, 20, 22].

The electrical resistance as a function of temperature  $R(T)$ , between low and room temperature, of the studied samples is shown in Fig. 2. There, the residual resistance ratio ( $RRR = R_{300K}/R_{8K}$ ) is indicated. The  $RRR$  value

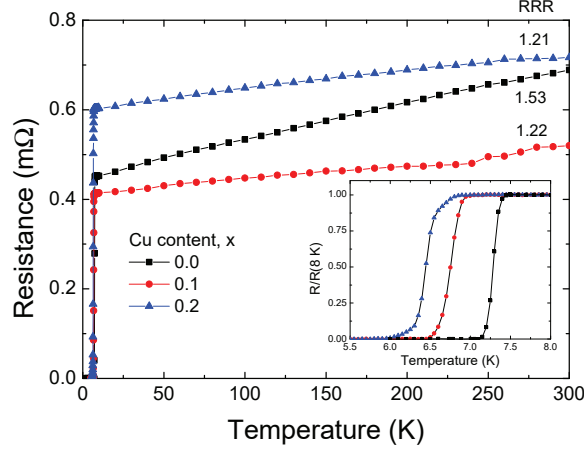


Figure 2: (Color online) Electrical resistance as a function of temperature of  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  samples. The residual resistance ratio ( $RRR$ ) is indicated for each sample. The inset shows the low temperature normalized resistance at 8 K, there the superconducting transition is observed.

provides qualitative information about electron scattering by impurities and vacancies. The  $RRR$  values indicate that our samples have a big number of defects, probably included Li vacancies, because the low melting point of Li, and possibly substitutional Cu defects. Similar values of  $RRR$  were reported in  $\text{Li}_2\text{Pd}_3\text{B}$  polycrystalline samples with analogous  $T_C$  [5, 22], however samples of better quality, with  $RRR \sim 6.5$  and  $T_C \simeq 8$  K, has been reported [18].

The electrical resistance as a function of temperature measurements of  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  shows that  $T_C$  decreases as the Cu content increases. The inset in Fig. 2 shows the normalized resistance at 8 K, it is clear the Cu effect on the  $T_C$ . The critical temperature was determined at the middle of the transition.  $T_C$  values were 7.29 K, 6.75 K, and 6.44 K for samples with  $x=0.0$ , 0.1, and 0.2 respectively. The  $T_C$  value of the sample without Cu is between the values reported in the literature [11, 23, 24]. The transition temperature of  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  samples is sharp, with the width of the transition temperature  $\Delta T$  values between 0.16 and 0.45 K,  $\Delta T$  increases as the Cu content increases. A coarse estimation of the slope of  $T_C(x)$  is about -4.25 K/x, where  $x$  is the nominal at% Cu into the samples. Determining the slope of  $T_C(x)$  from the  $\text{Li}_2(\text{Pd}_{1-x}\text{Ni}_x)_3\text{B}$  [8] and  $\text{Li}_2(\text{Pd}_{1-x}\text{Pt}_x)_3\text{B}$  [22] data (in these cases  $x$  is the Ni or Pt content, respectively), we obtained -2 K/x and -5 K/x, respectively. From these values, it is clear that substitution of Pd with Cu or Pt produces a stronger decrement of  $T_C$  than the substitution of Pd with Ni. Then, a magnetic impurity into  $\text{Li}_2\text{Pd}_3\text{B}$  produces a weak decrement of  $T_C$  than a non magnetic impurity. This fact disagrees with the idea that  $\text{Li}_2\text{Pd}_3\text{B}$  is a conventional superconductor, where the magnetic impurities must have a strong effect in  $T_C$ .

The magnetoresistance measurements are shown in Fig. 3 for the three studied samples with applied fields from 0 to 40 kOe, as expected the critical temperature decreases as the magnetic field is increased. In the temperature range studied the lower  $T_C$  was determined at  $H = 30$  kOe, for higher fields  $T_C$  was not possible to determine because the temperature limit of the apparatus.

The upper critical field as a function of temperature was extracted from the curves of Fig. 3.  $H_{C2}(T)$  shows a linear behavior in the temperature range measured, see Fig. 4(a). The linear extrapolation at  $T=0$  K gives values of  $H_{C2}(0)$  between 48 to 54 kOe, with the higher value for sample with  $x=0.1$ . Figure 4(b) shows the reduced upper critical field  $h^*$  versus the reduced temperature  $t = T/T_C$ , for the three studied samples. To plot these data we used the equation proposed by WHH [16, 17]:

$$h^* = \frac{H_{C2}(t)}{\left(-\frac{dH_{C2}}{dt}\right)_{t=1}}. \quad (1)$$

It is noteworthy the linear behavior of the experimental data between  $t = 1$  and  $t \simeq 0.3$  and those almost collapse in one line. Similar linear behavior was observed in  $\text{Li}_2(\text{Pd}_{1-x}\text{Ni}_x)_3\text{B}$  but in a reduced temperature range, from  $t = 1$  to  $t \simeq 0.6$  [5]. To get information about the Cooper pairs breaking, we compare the experimental data with the WHH

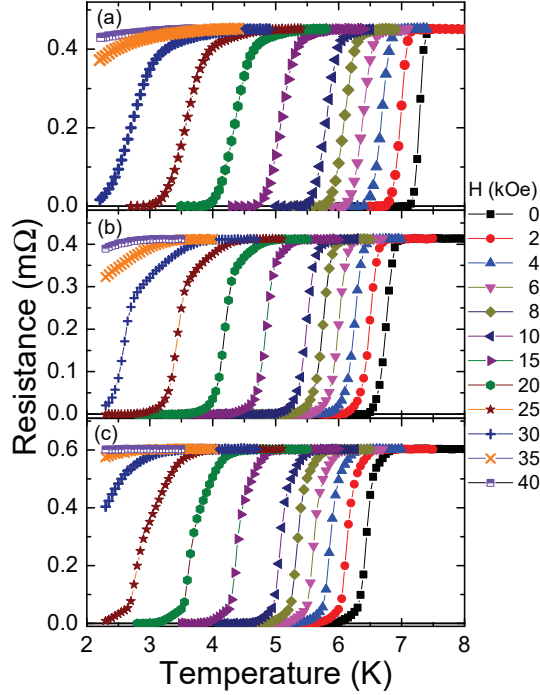


Figure 3: (Color online) Electrical resistance as a function of temperature and magnetic field for  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$ , (a)  $x=0.0$ , (b)  $x=0.1$  and (c)  $x=0.2$ . The symbols identify the applied magnetic field and are the same for the three panels.

theory (continuous line Fig. 4(b)). This curve was calculated according with [17],

$$\ln \frac{1}{t} = \sum_{\nu=-\infty}^{\infty} \left\{ \frac{1}{|2\nu+1|} - \left[ |2\nu+1| + \frac{\bar{h}}{t} + \frac{(\alpha\bar{h}/t)^2}{|2\nu+1| + (\bar{h} + \lambda_{SO})/t} \right]^{-1} \right\}, \quad (2)$$

in this equation  $\bar{h}$  is a dimensionless upper critical magnetic field,  $\alpha$  is the Maki parameter and  $\lambda_{SO}$  is the spin-orbit scattering,  $\alpha$  and  $\lambda_{SO}$  were taken as zero. It is clear that the experimental data deviate from the WHH prediction. Under this condition the spin-orbit scattering and pair breaking due to Pauli paramagnetism may be considered negligible.

The upper critical field at 0 K of the samples was determined in the approximation proposed in the WHH theory [16, 17];

$$H_{C2}^{WHH}(0) = -0.693T_C \left( \frac{dH_{C2}}{dT} \right)_{T=T_C} \quad (3)$$

The  $H_{C2}^{WHH}(0)$  values obtained for  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  are shown in Table 1. These values are slightly lower than the values reported for  $\text{Li}_2\text{Pd}_3\text{B}$  [18, 25, 26]. Samples where Pd was partially replaced with Ni shown that  $H_{C2}(0)$  and  $T_C$  decrease as the Ni content increases. The  $H_{C2}(T)$  of these samples is almost linear [5]. Substitution of a nonmagnetic impurity, to produce  $\text{Li}_2\text{Pd}_3\text{B}_{1-x}\text{Al}_x$  samples ( $x=0.0-0.1$ ), shown small  $T_C$  decrements and an increment of  $H_{C2}(0)$ , until 1.5 times. The  $T_C$  as a function of Al content or residual resistivity does not show a tendency. The upper critical field increment is attributed to impurities and defects, based on the residual resistivity, in fact the sample with the poor quality shown the higher  $H_{C2}(0)$  and correspond to the sample without Al [11].

The Ginzburg-Landau equation,  $H_{C2}(0) = \Phi_0(2\pi\xi_0^2)^{-1}$ , relates the upper critical field with the coherent length  $\xi_0$ . In this equation  $\Phi_0 = h/2e = 2.078 \times 10^{-15} \text{ T m}^2$  is the quantum fluxoid. Using the  $H_{C2}^{WHH}(0)$  values, we estimated  $\xi_0$ , the results where included in Table 1. Similar values were reported previously for  $\text{Li}_2\text{Pd}_3\text{B}$  [11, 21, 27].

Two non expected behavior has been observed in the  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  samples. The first one is a higher decrement of  $T_C$  with the Cu content, as compared with  $\text{Li}_2\text{Pd}_3\text{B}$  where Pd was substituted by Ni, a magnetic element. The second

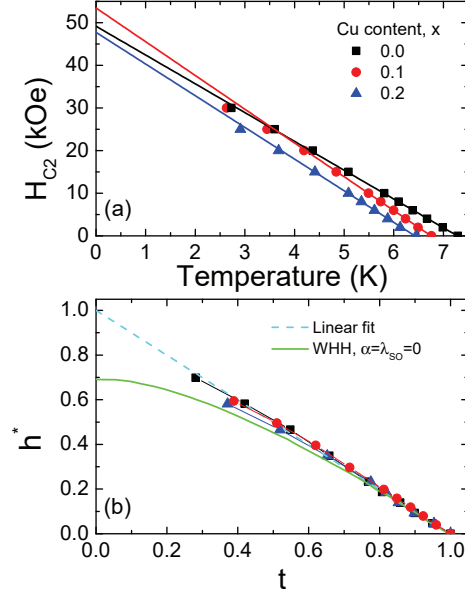


Figure 4: (Color online) (a) Upper critical field as a function of temperature of  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  ( $x=0.0, 0.1$  and  $0.2$ ). The lines are a linear fit of the data near to  $T_C$  (b) Normalized upper critical field  $h^*$  as a function of normalized temperature  $t = T/T_C$ . Continuous line represents the WHH model calculated with  $\alpha = \lambda_{SO} = 0$ . The dashed line is a linear fit of data near  $t = 1$  extrapolated to  $t = 0$ .

Table 1: Superconducting critical temperature  $T_C$ , slope of  $H_{C2}(T)$  at  $T = T_C$  and upper critical field  $H_{C2}$  at  $T=0$  K determined by the WHH approximation for  $\text{Li}_2\text{Pd}_{3-x}\text{Cu}_x\text{B}$  samples. The coherent length at  $T = 0$ ,  $\xi_0$ , is included.

Cu content $x$	$T_C$ (K)	$-(\frac{dH_{C2}}{dT})_{T=T_C}$ (kOe/K)	$H_{C2}^{WHH}(0)$ (kOe)	$\xi_0$ (nm)
0.0	7.29	6.75	34.1	9.84
0.1	6.75	7.92	37.0	8.91
0.2	6.44	7.43	33.1	9.96

unexpected behavior is an enhancement of the  $H_{C2}(T)$  at low temperatures that deviates from the WHH theory. This enhancement has been related to different causes; strong electron-phonon coupling [28], anisotropic Fermi surface [29] and localization effects in highly disordered superconductors [30]. The intensity of the electron-phonon coupling can be known from the BCS ratio  $2\Delta/K_B T_C = 3.52$ , indicative of weak coupling, or from the electron-phonon coupling constant  $\lambda_{e-ph}$ .  $2\Delta/K_B T_C$  values between 3.94 and 4.5 [31–33] and  $\lambda_{e-ph}$  values between 0.74 and 1.09 [5, 31, 34] have been reported for  $\text{Li}_2\text{Pd}_3\text{B}$ . These values indicate that  $\text{Li}_2\text{Pd}_3\text{B}$  is an intermediate coupling superconductor. Then the  $H_{C2}(T)$  enhancement may be because this characteristic. However some grade of disorder could be present due to a high number of defects, as indicated by the RRR values, then disorder could be participating in the enhancement of  $H_{C2}(T)$ . It is clear that more work is required to explain this behavior, particularly it is necessary to know the possible role of Li vacancies in this problem.

#### 4. Conclusions

In summary, we reported the effects of partial substitution of Pd with Cu in  $\text{Li}_2\text{Pd}_3\text{B}$  on the superconducting critical temperature and on the upper critical field. The results shown that  $T_C$  decreases as the Cu content is increased, with a slope of  $T_C(x)$  of  $-4.25$  K/x. The decrement of  $T_C$  with Cu content is faster than the decrement produced by a magnetic impurity, suggesting that  $\text{Li}_2\text{Pd}_3\text{B}$  may be considered an unconventional superconductor. The upper critical

field, at low temperature, is enhanced as compared with the WHH theory, without Pauli paramagnetism and spin-orbit scattering pair breaking contribution.

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